

# **Effect of Ligand Coordination on Complex Formation: Synthesis & Structural Studies of metal(I) salts containing the N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub> and OTeF<sub>5</sub> groups**



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## *Coworkers & Collaborators*



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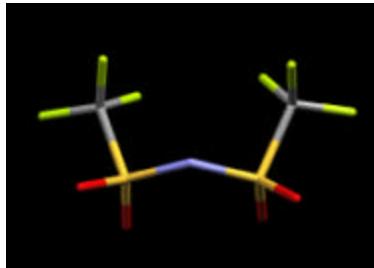
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### **Dr. Fook S. Tham**

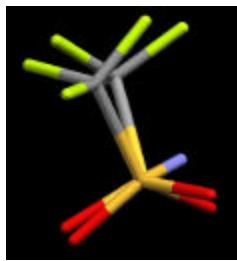
Department of Chemistry, University of California, Riverside CA 92521



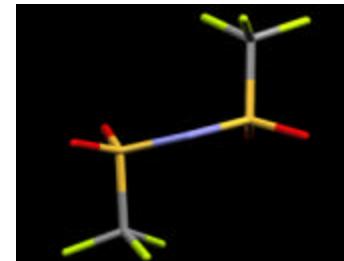
# Coordination & isomerism in $N(SO_2CF_3)_2$



**“Cisoid”**



**C-S--S-C  
“torsion”**



**“Transoid”**

- ✓ The “cisoid” form is less common. In the CCDC, only 6 structures show this conformation whereas the “transoid” form occurs in 15 remaining structures
- ✓ The “cisoid” conformation results from stronger cation-anion interaction
- ✓ The “cisoid” exclusively when anion is chelated to the metal center
- ✓ The “transoid” form dominates in structures containing a “free” anion
- ✓ NO structure known with both “cisoid” AND “transoid” geometry

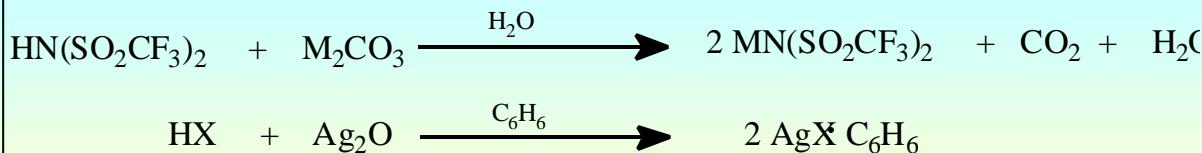
**DesMarteau, Pennington *et al.*, Solid State Sciences, 2002, 4, 1535-**

**1545**

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## Synthesis of metal(I) derivatives



These salts are colorless crystalline materials. Some turn amorphous with time

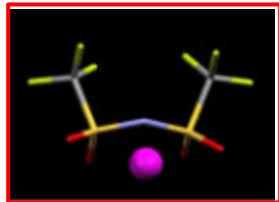
nTe-O ( $\text{cm}^{-1}$ ): IR (Ra) at ~865 (860)  
n<sub>as</sub> SO<sub>2</sub> ( $\text{cm}^{-1}$ ): IR (Ra) at ~1320(~1328)

<sup>1</sup>H NMR: C<sub>6</sub>H<sub>6</sub> peak at 7.6-7.7 ppm  
Uncoordinated benzene: 7.3  
<sup>19</sup>F NMR: ~-78 ppm (CF<sub>3</sub>)

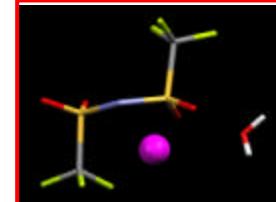
- ✓ These salts are colorless and crystalline.
- ✓ Recrystallization from iso-propylalcohol gave anhydrous salts.
- ✓ Some of these salts turn amorphous with time



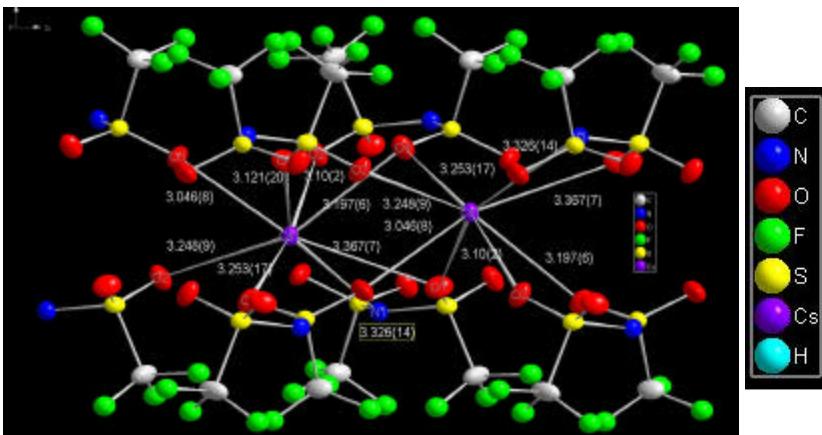
# **Structure of $CsN(SO_2CF_3)_2$ salts**



# CsN(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>



## CsN(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>•H<sub>2</sub>O

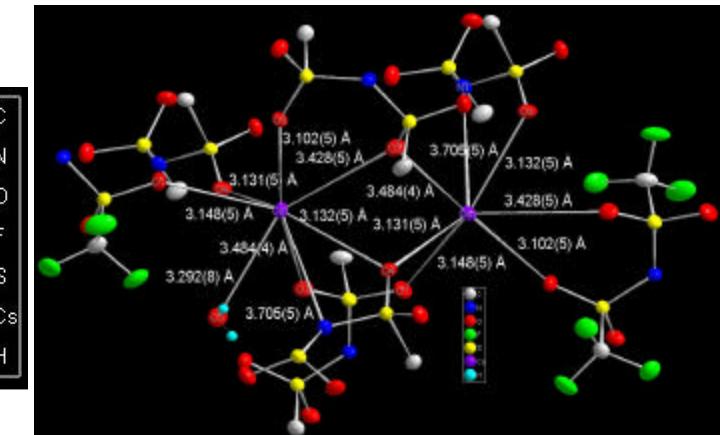


## Monoclinic $C2/c$ [ $\beta = 91.92(1)^\circ$ ]

$a = 22.509(12)$ ,  $b = 7.029(4)$ ,  $c = 13.519(7)$  [Å]

**Volume (Å<sup>3</sup>) = 2137.5(19), Z = 8, T = 298 K**

R1 = 0.0399, S = 1.024



Tetragonal *I*-4

$$a = 16.903(1), c = 7.8933(6) \text{ [Å]}$$

**Volume (Å<sup>3</sup>) = 2255.2(3), Z = 6, T = 298 K**

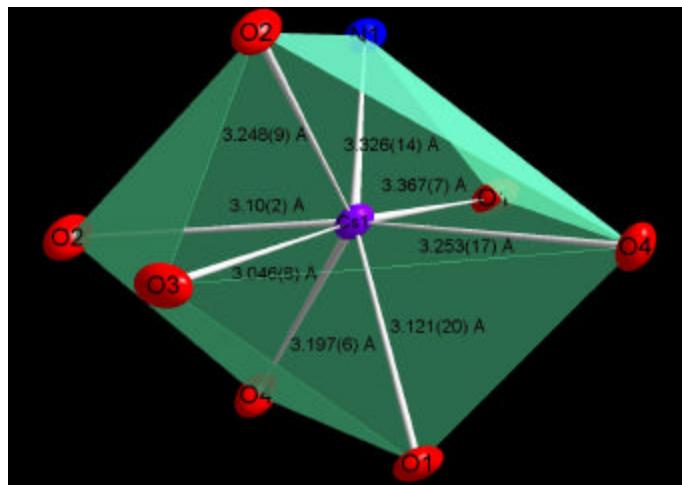
R1 = 0.0307, S = 1.20



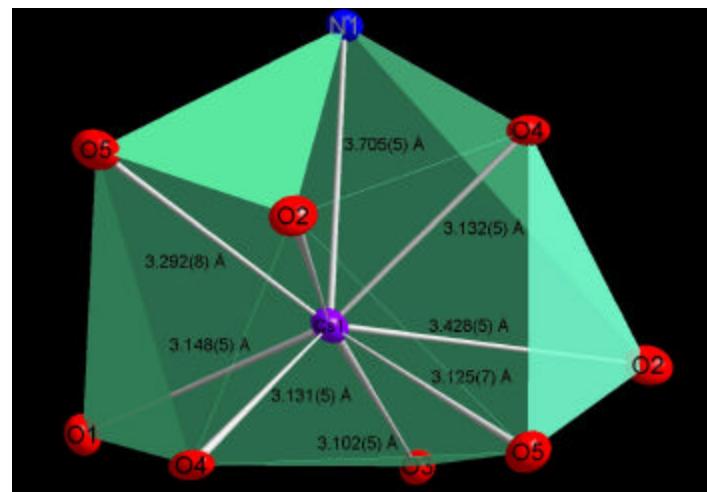
# Coordination environment of Cs in $\text{CsN}(\text{SO}_2\text{CF}_3)_2$ salts



Octa-coordinated with a short Cs-N bond



Nona-coordinated with a long Cs-N bond

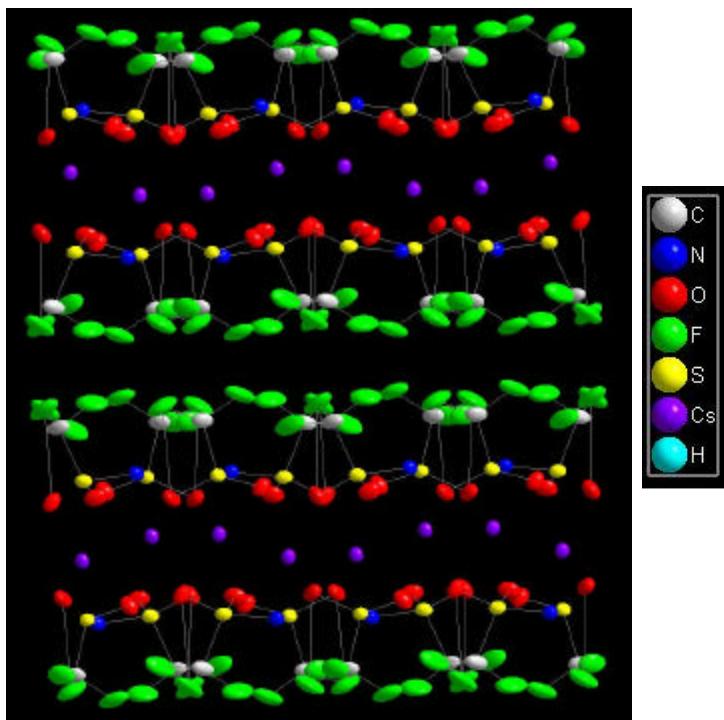




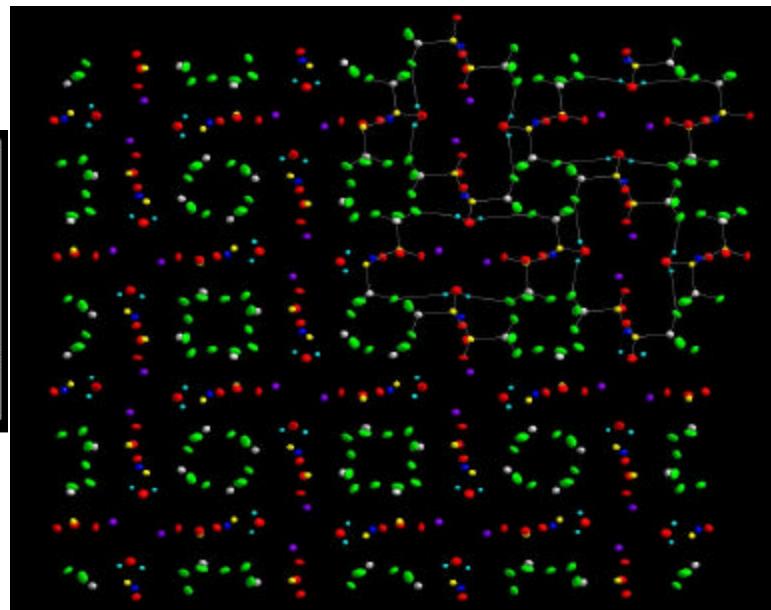
# *Crystal packing in $CsN(SO_2CF_3)_2$ salts*



Hydrophobic and hydrophilic Layering

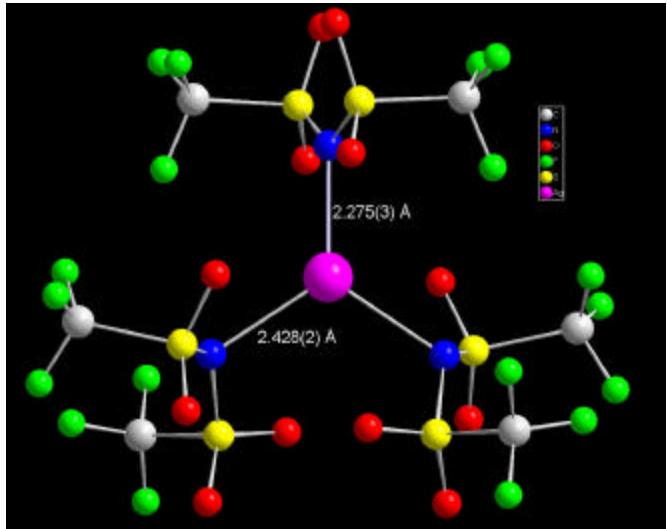


“Swiss cheese” Tunnel/channel structure





# Polymorphism in $\text{AgN}(\text{SO}_2\text{CF}_3)_2$



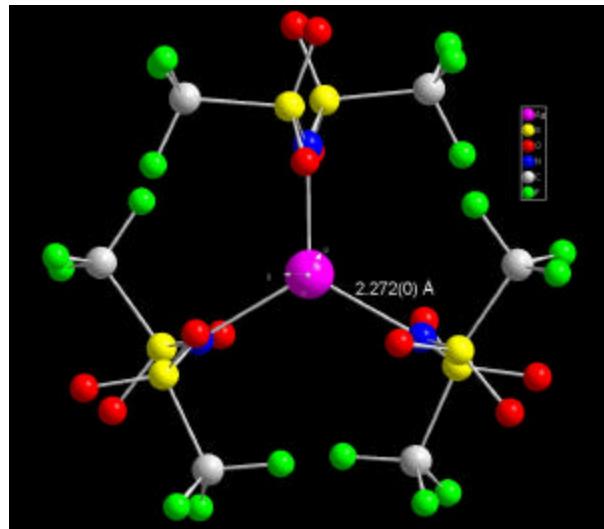
## Unit cell dimensions ( $\text{\AA}$ )

Orthorhombic  $P2_1/n$

$a = 7.510(6)$ ,  $b = 15.729(12)$ ,  $c = 8.119(7)$

Volume ( $\text{\AA}^3$ ) =  $876.7(12)$ ,  $Z = 4$ ,  $T = 298 \text{ K}$

$R1 = 0.1028$ ,  $S = 1.84$



## Unit cell dimensions ( $\text{\AA}$ )

Trigonal  $P-3_1c$

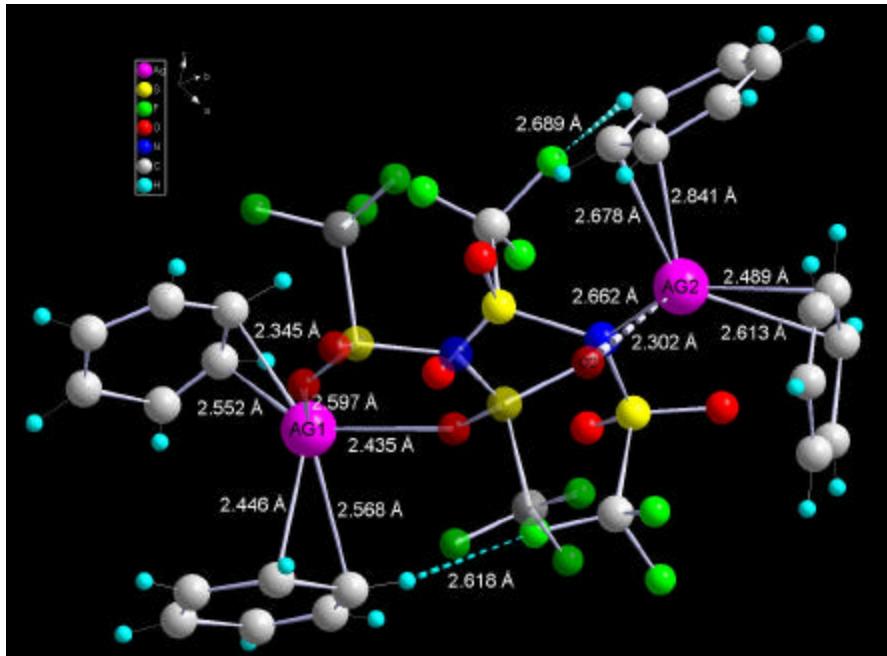
$a = 7.510(6)$ ,  $c = 8.119(7)$

Volume ( $\text{\AA}^3$ ) =  $876.7(12)$ ,  $Z = 6$ ,  $T = 298 \text{ K}$

$R1 = 0.1028$ ,  $S = 1.84$



# Structure of $[AgN(SO_2CF_3)_2(C_6H_6)_2]$



- ✓ Dimerization via S-O...Ag bonding (2.302 Å)
- ✓ Long unsymmetrical Ag-C bonds
- ✓ N( $SO_2CF_3)_2$  group is “transoid”
- ✓ H...F bond distances observed close to sum of van der Waal distance

Triclinic  $P\bar{1}$

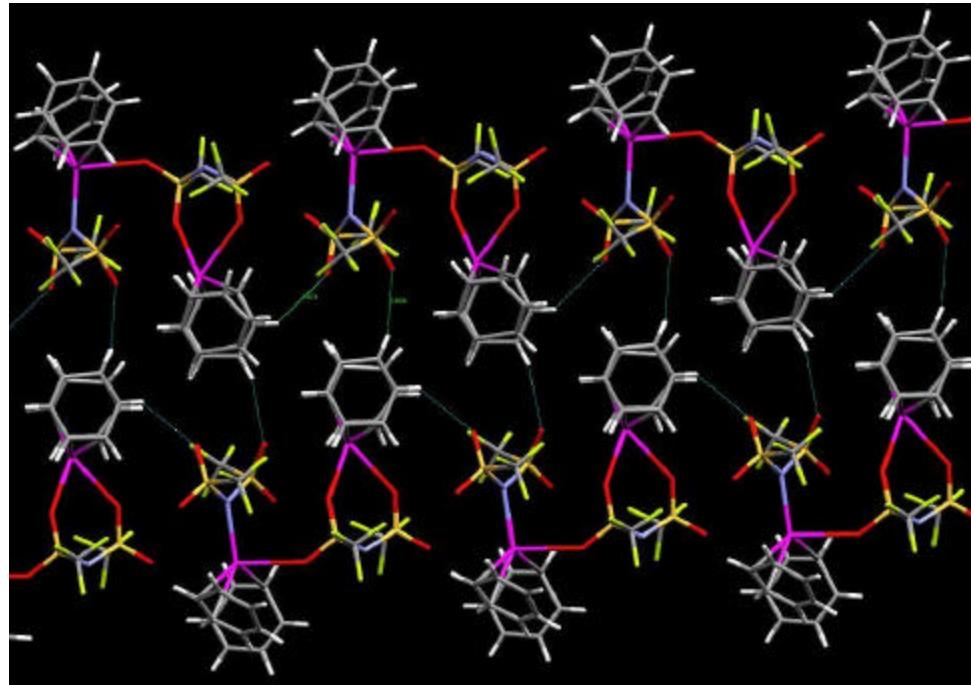
$a = 7.6704(13)\text{\AA}$ ,  $b = 8.4295(14)\text{\AA}$ ,  $c = 8.8631(15)\text{\AA}$ ,

$\alpha = 111.673(3)^\circ$ ,  $\beta = 108.479(3)^\circ$ ,  $\gamma = 97.798(3)^\circ$

$V (\text{\AA}^3) = 483.89(14)$ ,  $Z = 2$ ,  $T = 298(2) K$ ;  $R1 = 0.0432$ ,  $S = 1.114$

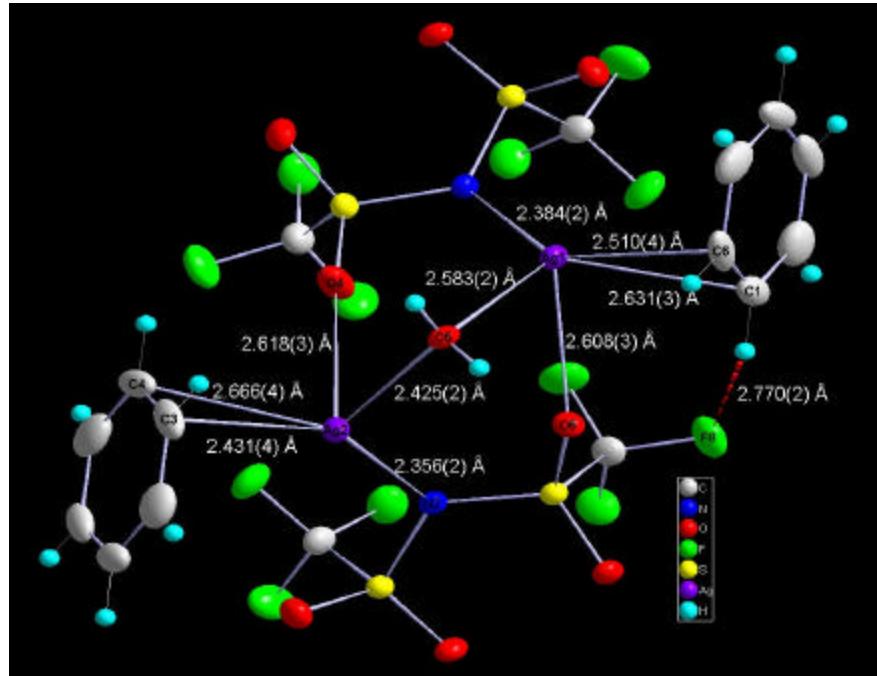


# *Crystal packing in [AgN(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>(C<sub>6</sub>H<sub>6</sub>)<sub>2</sub>]*





# Structure of [AgN(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>(C<sub>6</sub>H<sub>6</sub>)]<sub>2</sub>•H<sub>2</sub>O



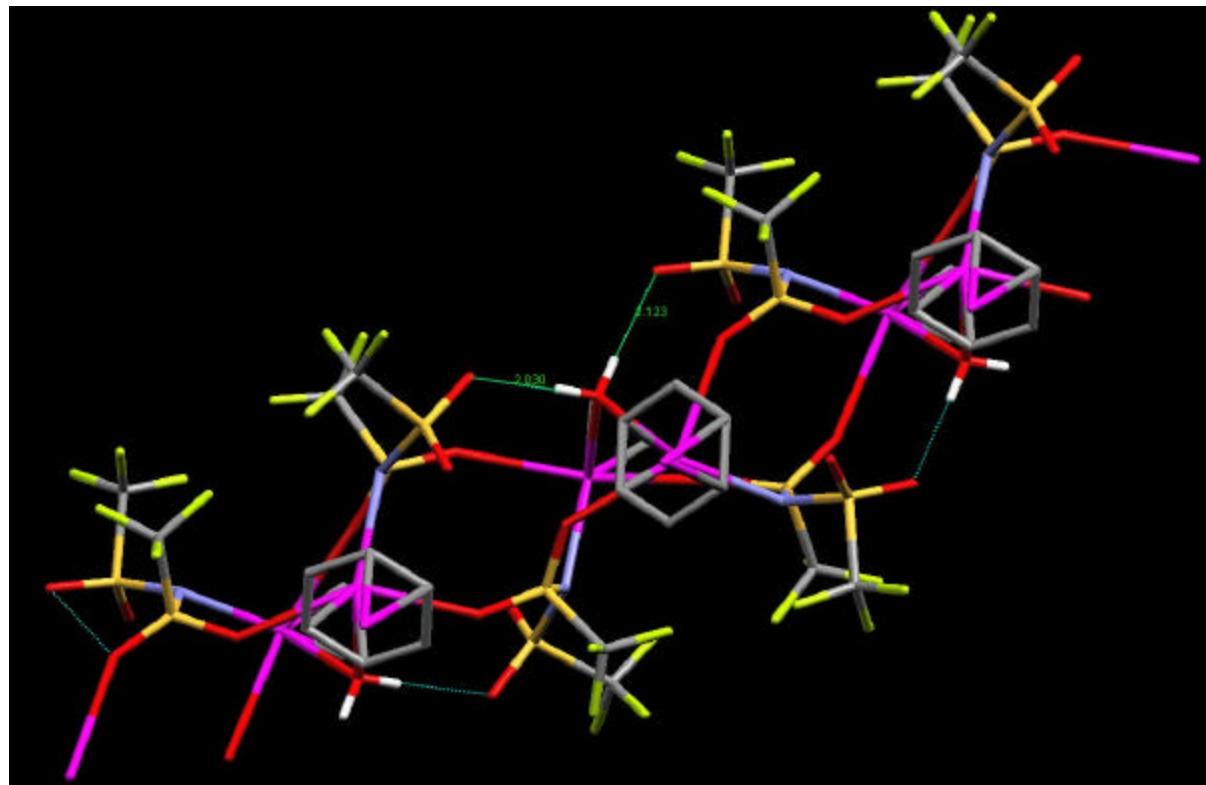
Monoclinic  $P2_1/n$

$a = 10.372(1)\text{\AA}$ ,  $b = 19.823(2)\text{\AA}$ ,  $c = 12.406(1)\text{\AA}$ ,  $\beta = 108.536(3)$ °,  
 $V (\text{\AA}^3) = 2148.5(5)$ ,  $Z = 8$ ,  $T = 173(1)$  K;  $R1 = 0.0224$ ,  $S = 1.04$

- ✓ N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub> group is both N- as well as O-bonded to silver
- ✓ Water bridges the eighth-membered Ag-O-S-N-Ag-O-S-N ring forming two fused six-membered rings.
- ✓ Unsymmetrical Ag-C bonds
- ✓ N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub> group is “cisoid”
- ✓ H...F bond distances observed close to sum of van der Waal distance



# *Crystal packing in [AgN(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>(C<sub>6</sub>H<sub>6</sub>)]<sub>2</sub>•H<sub>2</sub>O*



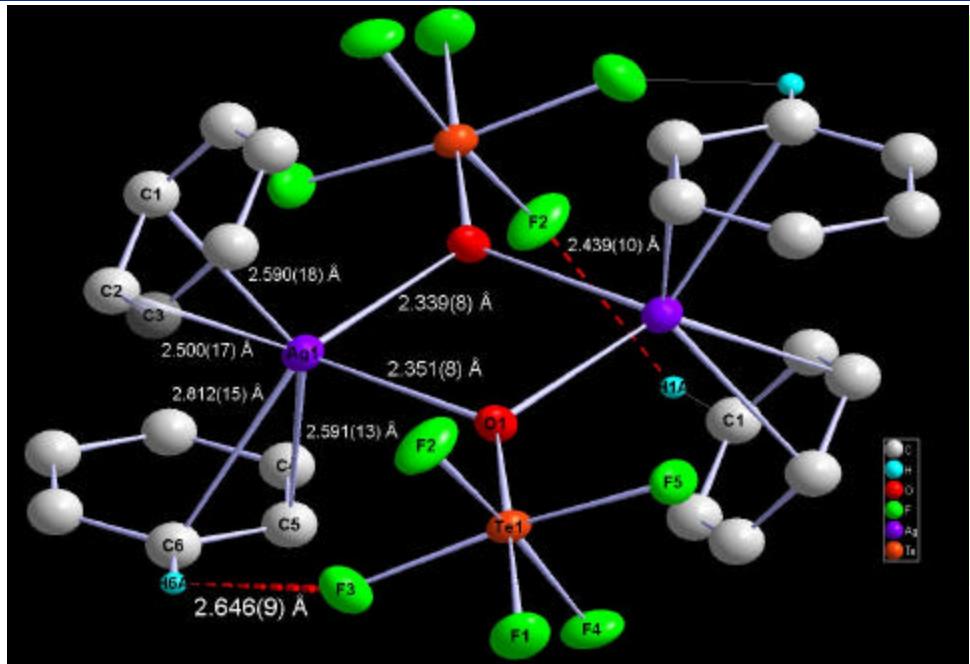
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# Structure of $[AgOTeF_5(C_6H_6)_2]_2$



- ✓ Dimeric structure
- ✓ Unsymmetrical Ag-C bonds
- ✓ Unsymmetrical and very long Te-O bonds
- ✓ H...F bonds observed

Triclinic  $P\bar{1}$

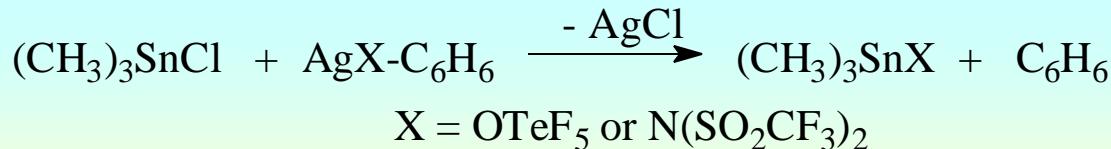
$$a = 7.6704(13)\text{\AA}, b = 8.4295(14)\text{\AA}, c = 8.8631(15)\text{\AA},$$

$$\alpha = 111.673(3)^\circ, \beta = 108.479(3)^\circ, \gamma = 97.798(3)^\circ$$

$$V (\text{\AA}^3) = 483.89(14), Z = 2, T = 298(2) K; R1 = 0.0432, S = 1.114$$



## Reaction of silver salts: Synthesis of trimethyltin(IV) derivatives



MS shows  $[\text{M}-\text{CH}_3]^+$  peak

Trimethyltin(IV) teflate can be distilled at 50 °C under vacuum (0.1 T)

$\text{nTe-O}$  ( $\text{cm}^{-1}$ ): IR (Ra) at 860 (856)  
 $\text{nSn-C}$  ( $\text{cm}^{-1}$ ) IR (Ra): asym: 552 (554); sym 518 (518)

$\text{n}_{\text{as}}\text{SO}_2$  ( $\text{cm}^{-1}$ ): IR (Ra) at 1342(1327)  
 $\text{nSn-C}$  ( $\text{cm}^{-1}$ ) IR (Ra): asym: 558 (556); sym 520 (513)

$\text{nTe-O}$  ( $\text{cm}^{-1}$ )  $\text{F}_5\text{TeOCl}$ : IR (Ra) at 551 (554);  $\text{nTe-O}$  ( $\text{cm}^{-1}$ )  $\text{F}_5\text{TeOTBA}$ : IR (Ra) at 867 (866);

- ✓ Trimethyltin(IV) derivatives are colorless viscous oils.
- ✓ Highly moisture sensitive
- ✓ Potentially stronger catalysts in organic synthesis compared to TMSOTf



## *What is so interesting about $(CH_3)_3Sn$ derivatives of strong acids??*



- ✓ The Sn-C bond cleavage can be selective i.e., there is a competition between Sn-C and Sn-Cl bond cleavage depending upon the acid used.
- ✓ The trimethyltin(IV) derivatives of strong acids are extremely electrophilic reagents that have application in organic synthetic reactions.

- ✓ The electrophilic nature of an organotin(IV) compound can be reflected by its  $^{119}Sn$  chemical shift i.e., deshielding.  $^{119}Sn$  has a spin of  $\frac{1}{2}$ , relative abundance of 8.58 % and has high relative sensitivity (30x  $^{13}C$ ).
- ✓ Can  $^{119}Sn$  chemical shifts (in neat liquids or as a solution in “low-coordinating” solvents) be correlated to anion basicities in case of trimethy tin(IV) derivatives?



## Correlating spectroscopy and crystallography



Correlation of  ${}^2J({}^{119}\text{Sn}-{}^1\text{H})$  and C-Sn-C angle (determined from x-ray crystallography gives the following non-linear relationship:

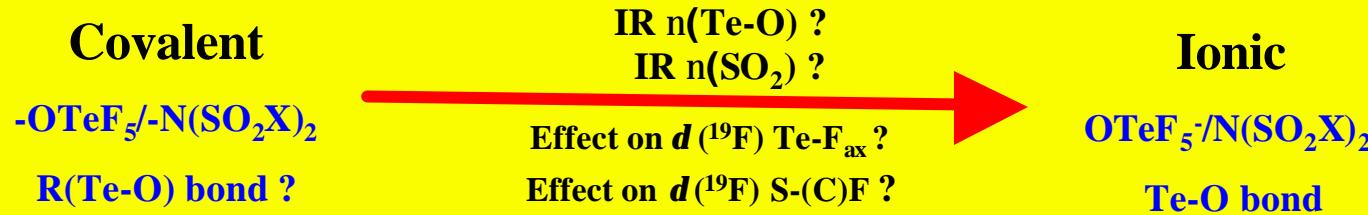
$$T (\text{C-Sn-C})^\circ = 0.0161 |{}^2J({}^{119}\text{Sn}-{}^1\text{H})|^2 - 1.32 |{}^2J({}^{119}\text{Sn}-{}^1\text{H})| + 133.4$$

Correlation of  ${}^1J({}^{119}\text{Sn}-{}^{13}\text{C})$  and C-Sn-C angle (determined from x-ray crystallography gives the following linear relation:

$$11.4T - 875 = |{}^1J({}^{119}\text{Sn}-{}^{13}\text{C})|$$

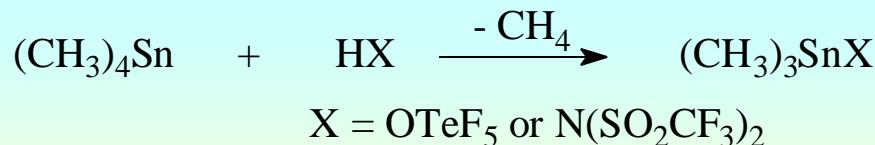
Lockhart, T. P.; Manders, W. F. *Inorg. Chem.* 1985, 25, 892

Lockhart, T. P.; Manders, W. F.; Zuckerman, J. J. *J. Am. Chem. Soc.* 1985, 107, 4546





## Synthesis of trimethyltin(IV) derivatives



MS shows [M-CH<sub>3</sub>]<sup>+</sup> peak

Trimethyltin(IV) teflate can be distilled at 50 °C under vacuum (0.1 T)

nTe-O (cm<sup>-1</sup>): IR (Ra) at 860 (856)  
nSn-C (cm<sup>-1</sup>) IR (Ra): asym: 552 (554); sym 518 (518)

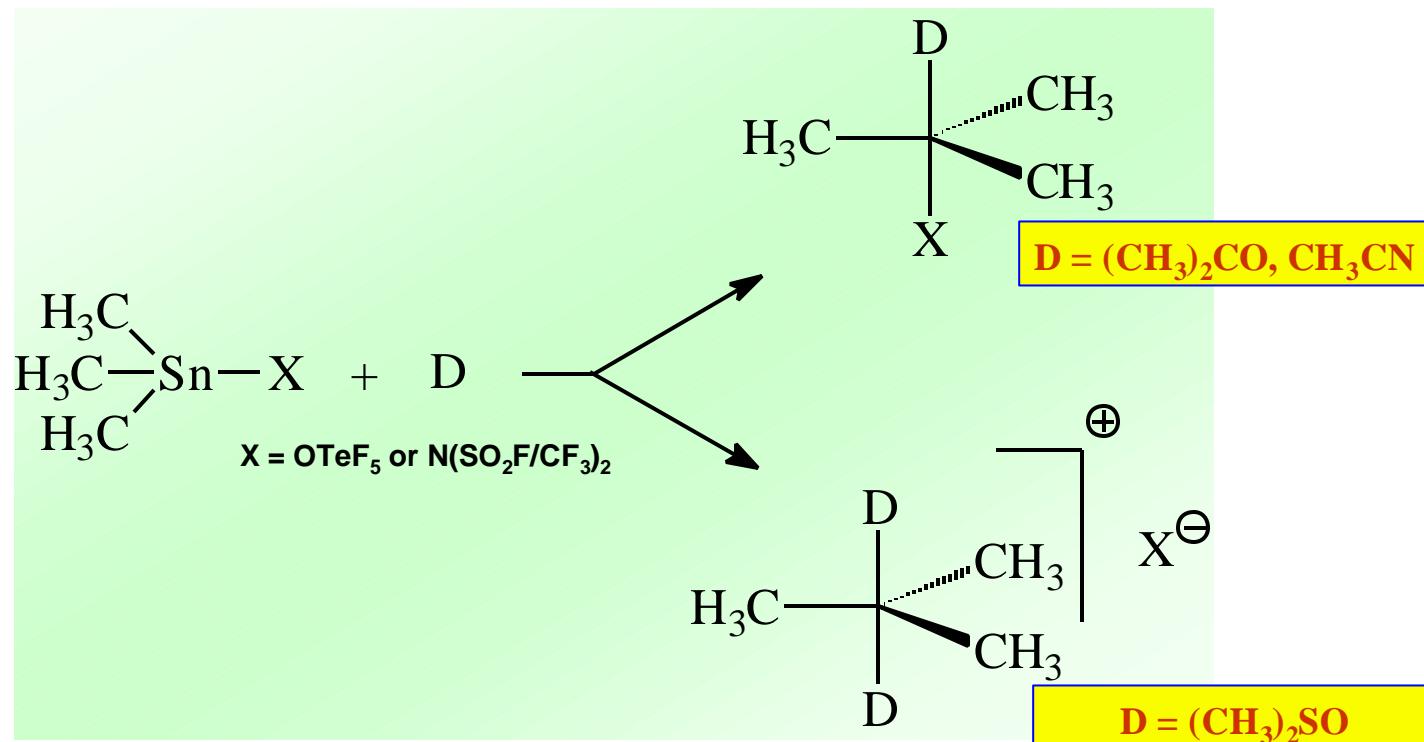
n<sub>as</sub>SO<sub>2</sub> (cm<sup>-1</sup>): IR (Ra) at 1342(1327)  
nSn-C (cm<sup>-1</sup>) IR (Ra): asym: 558 (556); sym 520 (513)

nTe-O (cm<sup>-1</sup>) F<sub>5</sub>TeOCl: IR (Ra) at 551 (554); nTe-O (cm<sup>-1</sup>) F<sub>5</sub>TeOTBA: IR (Ra) at 867 (866);

- ✓ Tetramethyltin is used in large excess
- ✓ Reaction by-products can be easily removed under vacuum
- ✓ Trialkyltin(IV) derivatives are colorless viscous oils that are highly sensitive to moisture and donor solvents.

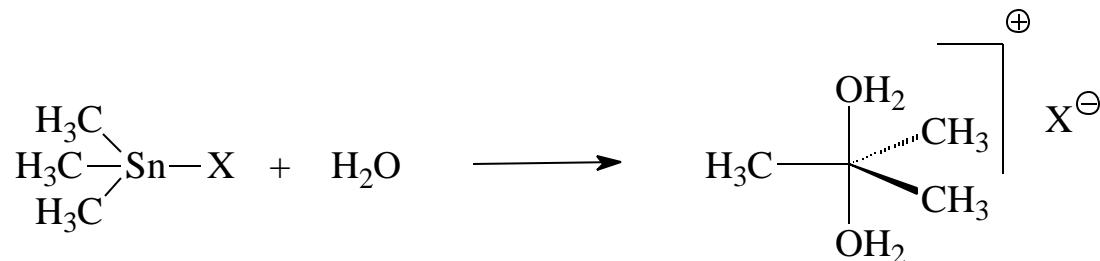


## Coordination complex formation with donor solvents



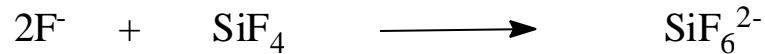
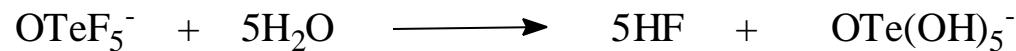


# *Formation of the hydrated trimethylstannyl cation*



The hydrated salt can be isolated with  $\text{N}(\text{SO}_2\text{CF}_3)_2$  anion but NOT for  $\text{OTeF}_5$  anion.

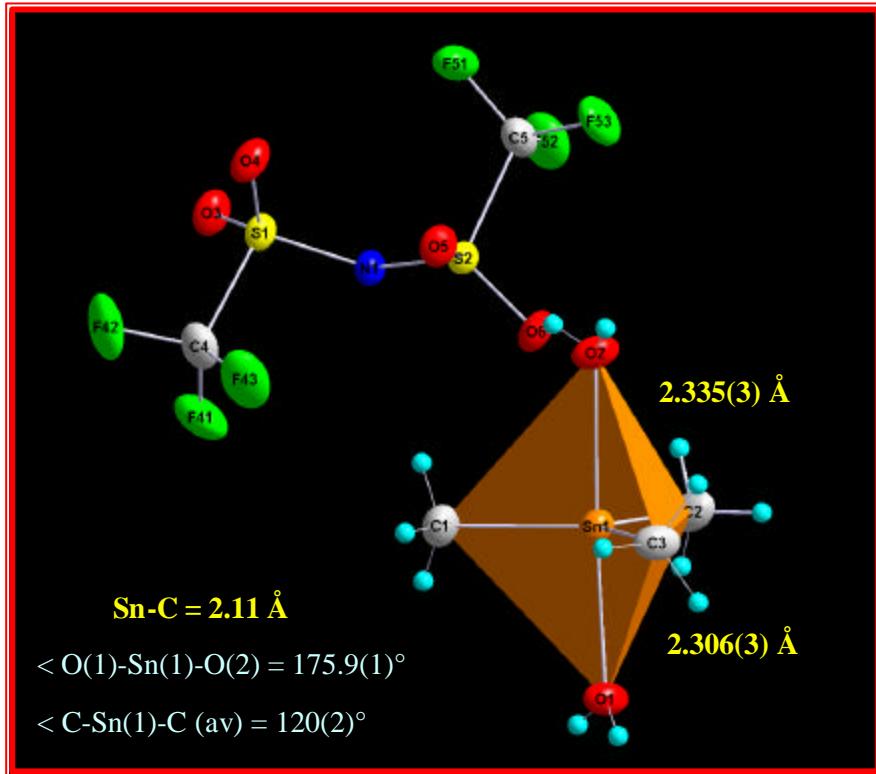
The compound isolated after hydrolysis is  $[\text{Me}_3\text{Sn}(\text{OH}_2)_2]_2\text{SiF}_6$



The hydrolysis of trimethyltin teflate results in the decomposition of the OTeF<sub>5</sub> group



# Hydrated trimethyltin(IV) cation



## Unit cell dimensions (Å)

Monoclinic ( $P2_1/c$ )

$a = 7.3072(1)$ ,  $b = 13.4649(2)$ ,

$c = 16.821(2)$

$\beta = 98.705(1)^\circ$

**Volume (Å<sup>3</sup>) = 1636.0(3)** ,

**Z = 4**

**T = 213(2)**

**R1 = 0.0367**

**wR2 = 0.0736**

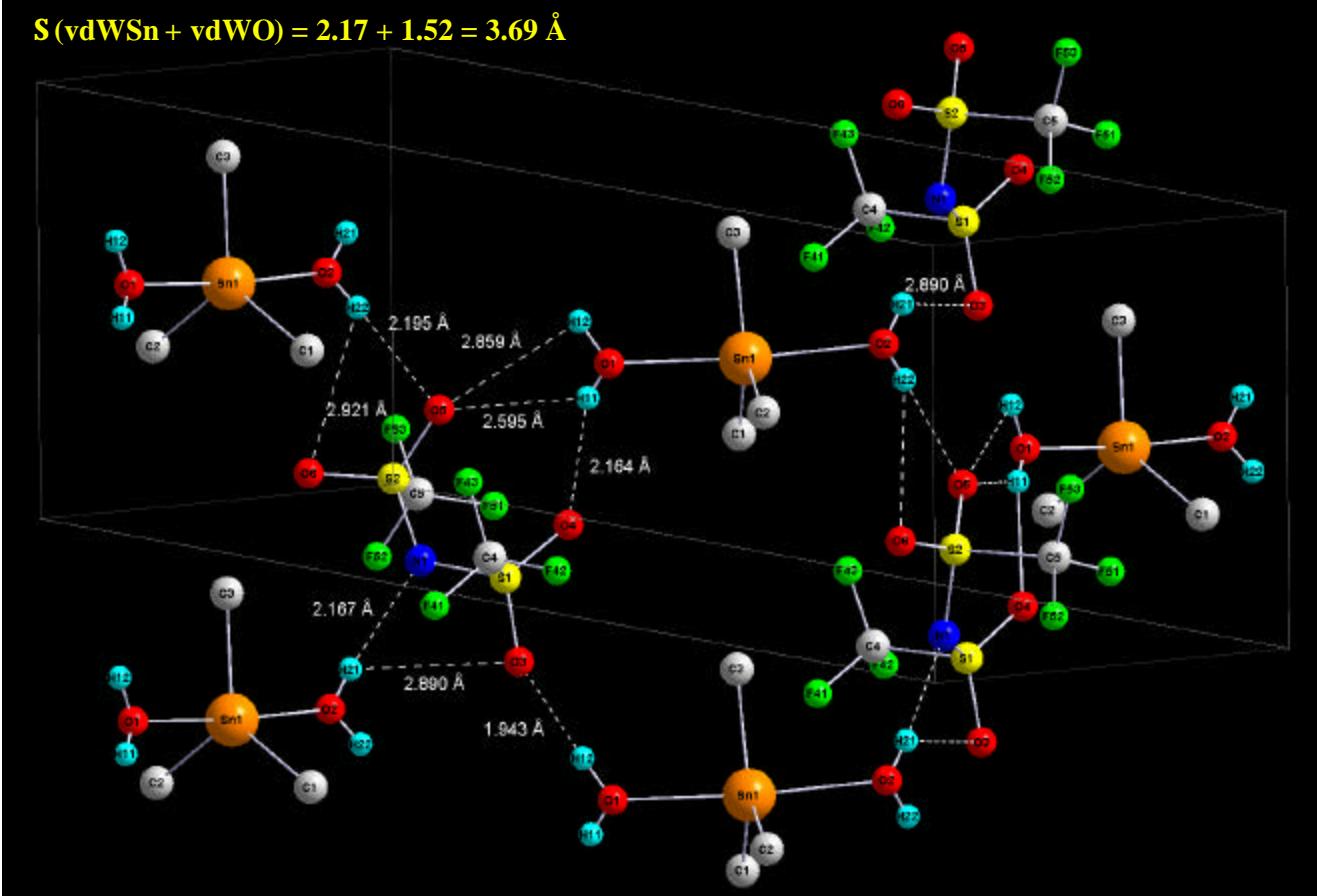
**S = 1.233**



# Hydrogen bonding in hydrated trimethyltin(IV) cations



$$S(vdWSn + vdWO) = 2.17 + 1.52 = 3.69 \text{ \AA}$$



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# Multinuclear NMR Parameters

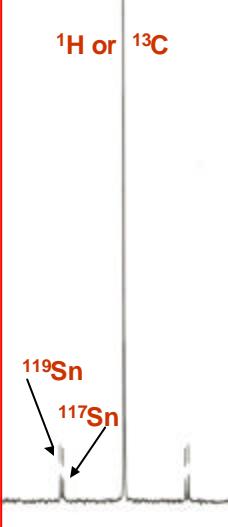


Table 1. <sup>1</sup>H, <sup>13</sup>C NMR Spectroscopic Data<sup>a</sup> and calculated<sup>b,c</sup> C-Sn-C angles for (CH<sub>3</sub>)<sub>3</sub>SnX [X = OTeF<sub>5</sub> and N(SO<sub>2</sub>F/CF<sub>3</sub>)<sub>2</sub>]

Solute	Solvent <sup>d</sup>	$\delta(^1\text{H})$ ppm	$^2J(^{119}(^{117})\text{Sn}-^1\text{H})$ Hz	$\theta(\text{C-Sn-C})$ <sup>b</sup> (°)	$\delta(^{13}\text{C})$ ppm	$^1J(^{119}(^{117})\text{Sn}-^{13}\text{C})$ Hz	$\theta(\text{C-Sn-C})$ <sup>c</sup> (°)
(CH <sub>3</sub> ) <sub>3</sub> SnOTeF <sub>5</sub>	neat	0.84	59.2 <sup>e</sup>	111.7	0.84	376.9(360.3)	109.8
	CH <sub>2</sub> Cl <sub>2</sub>	0.79	58.5(55.9)	111.3	0.90	374.0(357.4)	109.6
	acetone	0.69	68.8(65.8)	118.8	1.55	480.4(459.3)	118.9
	CH <sub>3</sub> CN	0.66	69.2(66.2)	119.2	1.49	484.6(463.1)	119.3
	DMSO	0.50	69.5(66.6)	119.4	1.05	511.4(490.0)	121.6
(CH <sub>3</sub> ) <sub>3</sub> SnOTeF <sub>5</sub>	AN/H <sub>2</sub> O	0.46	69.6(66.7)	119.5	0.10	508.5(486.0)	121.4
	DMSO/H <sub>2</sub> O	0.43	70.1(68.5) <sup>e</sup>	120.0	0.84	515.5(492.5)	122.0
(CH <sub>3</sub> ) <sub>3</sub> SnN(SO <sub>2</sub> F) <sub>2</sub>	neat	0.91	63.8(61.6)	114.7	1.6	416.8(400.3)	113.3
	CH <sub>2</sub> Cl <sub>2</sub>	0.96	62.3(59.9)	113.6	1.4	404.1(387.7)	112.2
(CH <sub>3</sub> ) <sub>3</sub> SnN(SO <sub>2</sub> CF <sub>3</sub> ) <sub>2</sub>	DMSO	0.83	72.4(70.0)	122.2	-0.2	528.3(509.9)	123.1
	neat	0.84	64.2(61.6)	115.0	2.1	412.6(394.1)	113.0
	CH <sub>2</sub> Cl <sub>2</sub>	0.81	64.4(61.8)	115.2	0.8	414.8(395.2)	113.0
	CH <sub>3</sub> CN	0.82	70.2(67.1)	120.1	-1.7	489.5(467.6)	119.7
	DMSO	0.48	69.0(67.4)	119.0	0.7	512.2(499.0)	121.6
[(CH <sub>3</sub> ) <sub>3</sub> Sn(H <sub>2</sub> O)][N(SO <sub>2</sub> CF <sub>3</sub> ) <sub>2</sub> ]	CH <sub>3</sub> CN	0.61	69.7(66.7)	119.6	0.10	491.8(470.0)	120.0
	DMSO	1.18	69.8(66.7)	119.7	0.92	512.9(497.2)	121.8

<sup>a</sup> NMR spectroscopic data were recorded at 300 K.

<sup>b</sup> Calc from relation:  $\theta = 0.0161 |^2J(^{119}\text{Sn}-^1\text{H})|^2 - 1.32 |^2J(^{119}\text{Sn}-^1\text{H})| + 133.4$ .

<sup>c</sup> Calc from relation:  $|^1J(^{119}\text{Sn}-^{13}\text{C})| = 11.4 \theta - 875$ .

<sup>d</sup> Acetone = (CD<sub>3</sub>)<sub>2</sub>CO, DMSO = (CD<sub>3</sub>)<sub>2</sub>SO.

<sup>e</sup> Calculated from center of unresolved <sup>119</sup>Sn, <sup>117</sup>Sn satellites ( $|J_{\text{obs}}| \times 1.023$ )



## Multinuclear NMR parameters ...continued



Table 2.  $^{19}\text{F}$ ,  $^{119}\text{Sn}$  and  $^{125}\text{Te}$  NMR Spectroscopic Data<sup>a</sup> of  $(\text{CH}_3)_3\text{SnX}$  [X = OTeF<sub>5</sub> and N(SO<sub>2</sub>F/CF<sub>3</sub>)<sub>2</sub>]

Solute	Solvent <sup>b</sup>	$\delta(^{19}\text{F})$ , ppm			$\delta(^{119}\text{Sn})$	$\delta(^{125}\text{Te})$	$\delta(^{13}\text{CF}_3)$	$\frac{1}{2}J(^{19}\text{F}_{\text{ax}}-^{19}\text{F}_{\text{eq}})$ , Hz			$^1J(^{13}\text{C}-^{19}\text{F})$
		$\text{F}_{\text{ax}}$	$\text{F}_{\text{eq}}$	CF <sub>3</sub> /SO <sub>2</sub> F	Hz			F <sub>ax</sub>	F <sub>eq</sub>	Hz	
$(\text{CH}_3)_3\text{SnOTeF}_5$	neat	-32.9	-41.9		182.5	270.8 <sup>c</sup>	569.5		3112	3540	
	CH <sub>2</sub> Cl <sub>2</sub>	-30.3	-38.5		183.0	272.4	564.6		3188	3550	
	acetone	-29.1	-40.6		180.0	96.0	574.9		3020	3558	
	CH <sub>3</sub> CN	-29.2	-40.8		179.0	84.2	575.0		3032	3556	
	DMSO	-16.2	-33.8		170.0	40.0	598.7		2712	3666	
$(\text{CH}_3)_3\text{SnN}(\text{SO}_2\text{F})_2$	neat			55.5		242.5					
	CH <sub>2</sub> Cl <sub>2</sub>			55.6		248.6					
	DMSO			52.5		32.9					
$(\text{CH}_3)_3\text{SnN}(\text{SO}_2\text{CF}_3)_2$	neat			-78.5		240.2		118.7		320.4	
	CH <sub>2</sub> Cl <sub>2</sub>			-78.8		251.0		118.1		319.8	
	CH <sub>3</sub> CN			-78.9		44.9		119.4		320.7	
	DMSO			-78.6		37.4		120.0		321.7	
$[(\text{CH}_3)_3\text{Sn}(\text{H}_2\text{O})_2][\text{N}(\text{SO}_2\text{CF}_3)_2]$	CH <sub>3</sub> CN			-79.0		59.0					
	DMSO			-79.1		42.8					

<sup>a</sup> NMR spectroscopic data were recorded at 300 K

<sup>b</sup> Acetone = (CD<sub>3</sub>)<sub>2</sub>CO, DMSO = (CD<sub>3</sub>)<sub>2</sub>SO

<sup>c</sup>  $^{119}\text{Sn}$  NMR shows a peak at 300.7 ppm in HOTEF<sub>5</sub>

$^{19}\text{F}_{\text{ax}}$  NMR for TEAOTeF<sub>5</sub> = -25.4 ppm

B(OTeF<sub>5</sub>)<sub>3</sub> = -46.2 (Strauss et al., 1986)



## *<sup>119</sup>Sn chemical shifts and anion basicity*



- *d* (<sup>119</sup>Sn) values lower (more downfield) than +200 ppm show a highly deshielded tin nuclei. Sometimes stronger acids results in relatively higher (upfield) chemical shifts due to close contacts even in solution state:

<u>Compound (Me<sub>3</sub>SnX)</u>	<u>d</u> ( <sup>119</sup> Sn)
X = ClO <sub>4</sub> (unidentate)	245
X = SO <sub>3</sub> CF <sub>3</sub> (bidentate)	162

**For trimethyltin(IV) derivate in dichloromethane solution  
the relative anion basicity can be ordered as:**





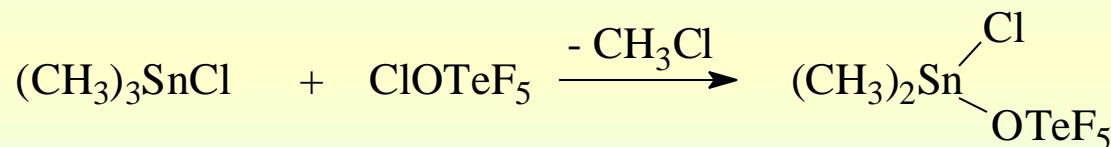
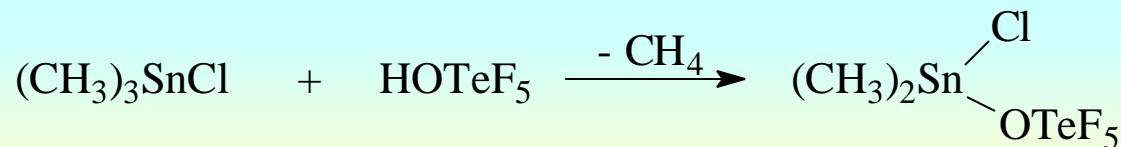
## ***Sn-C versus Sn-Cl bond cleavage***



**XN(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub> (X = H, Cl) shows a preferential Sn-Cl bond cleavage**



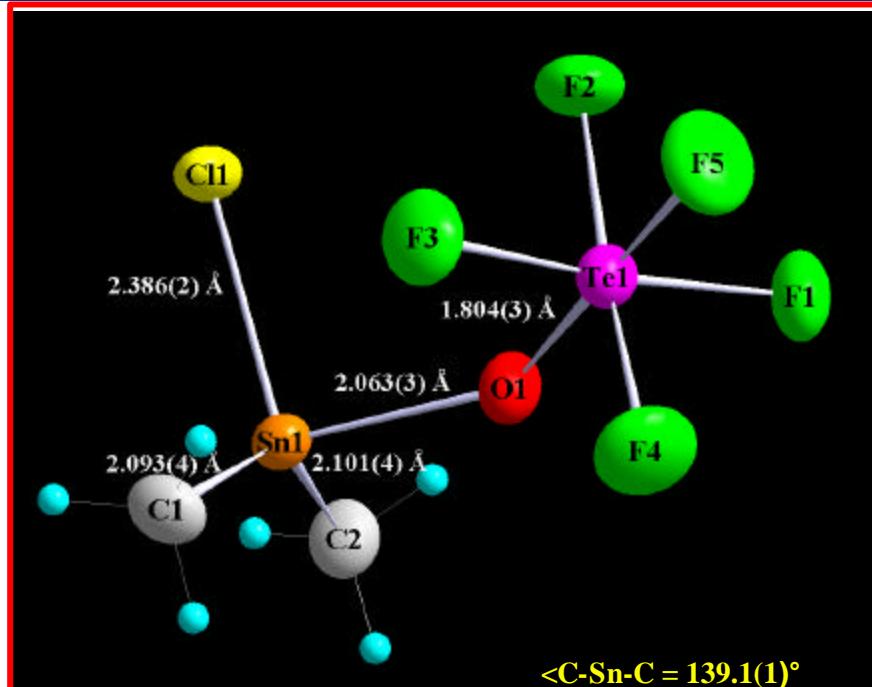
**XOTeF<sub>5</sub> (X = H, Cl) shows a preferential Sn-C bond cleavage**



**According to Sladky and Kropshofer (*JCS Chem. Commun.*, 1973, 600), reaction of (CH<sub>3</sub>)<sub>3</sub>SnCl with HOTeF<sub>5</sub> gives trimethyltin(IV) teflate exclusively!**



# Structure of $(CH_3)_2Sn(Cl)OTeF_5$



## Unit cell dimensions (Å)

Monoclinic  $P2_1/n$

$a = 5.8204(8)$ ,  $b = 10.782(1)$ ,

$c = 15.493(2)$

$\beta = 99.59(1)^\circ$

Volume ( $\text{\AA}^3$ ) = 971.7(2)

$Z = 4$

$T = 218(2) \text{ K}$

$R1 = 0.0282$

$wR2 = 0.0712$

$S = 1.088$

Te-O (Å) (X=OTeF<sub>5</sub>) : B(X)<sub>3</sub> = 1.874(6); [TBA][H(X)<sub>2</sub>] = 1.800(4)av; [Au(X<sub>3</sub>)<sub>2</sub>] = 1.91(2)

Strauss et al., *Inorg. Chem.*, 1986, 25, 2806 and references therein

n(TeO) = 856 cm<sup>-1</sup> in IR and Ra; n(SnO) = 427 (IR)/424 (Ra) cm<sup>-1</sup>; n(SnCl) = 313 (Ra) cm<sup>-1</sup>



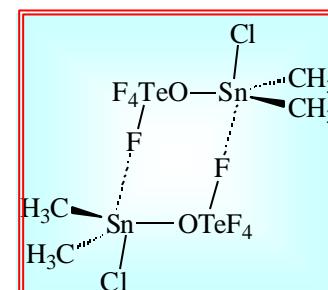
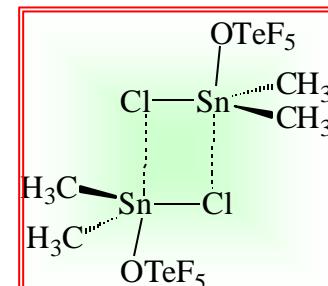
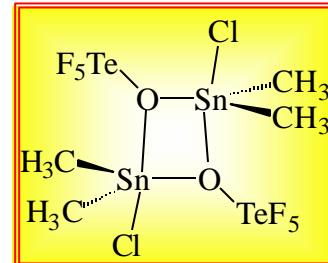
## Tetra- or pentacoordinated tin???



The C-Sn-C angle calculated using  $^2J(^{119}\text{Sn}-^1\text{H})$  (67.9 Hz) and  $^1J(^{119}\text{Sn}-^{13}\text{C})$  (472 Hz) coupling constants for  $(\text{CH}_3)_2\text{SnCl}(\text{OTeF}_5)$  dissolved in  $\text{CD}_2\text{Cl}_2$  is approximately  $\sim 118^\circ$ . The  $d(^{119}\text{Sn})$  value of  $\sim 142.7$  ppm indicates that tin is present in a five-coordinate environment. The fifth coordination site can be occupied by a bridging chlorine, fluorine or oxygen from a neighboring  $\text{Me}_2\text{SnCl}(\text{OTeF}_5)$  molecule .

$^{119}\text{Sn}$  NMR show the presence of another broad peak at  $\sim 127$  ppm, which is due to an equilibrium. In VT NMR studies using toluene- $d_8$  as a solvent, this peak disappears at  $-80^\circ\text{C}$ .

Mass spectrum shows  $[\text{M}-\text{CH}_3]^+$  peak as the highest peak indicating that the dimer is not stable in the gas phase

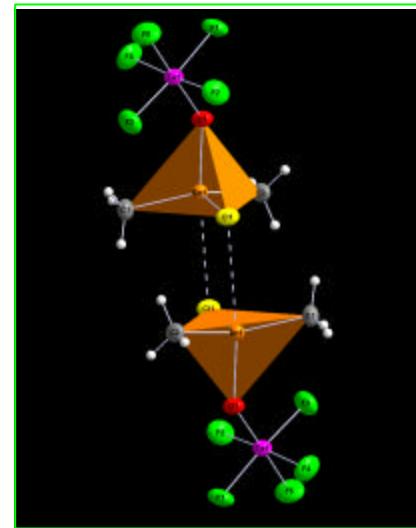
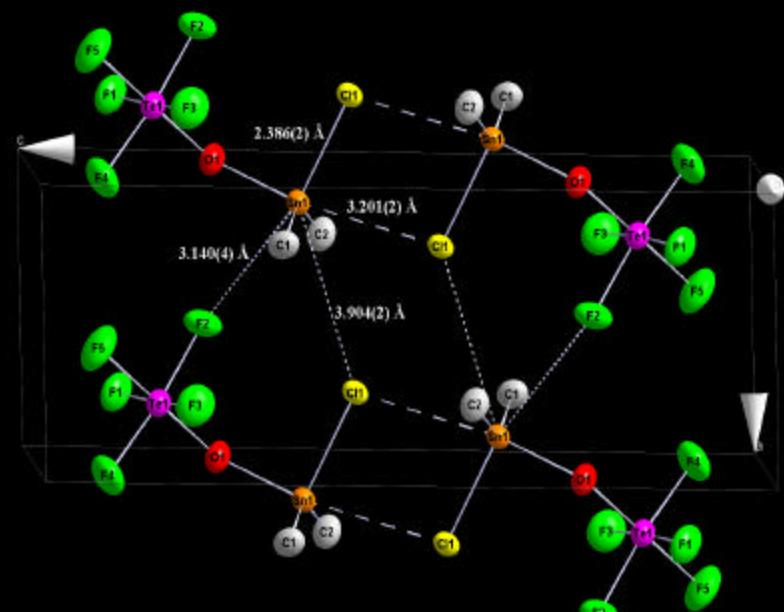




## Coordination environment around tin



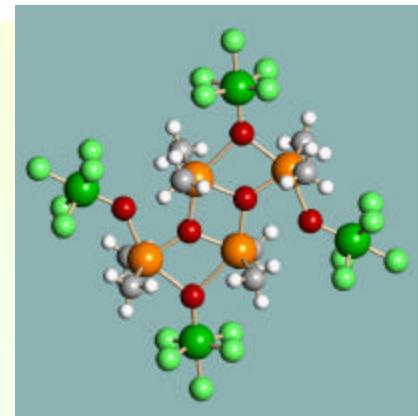
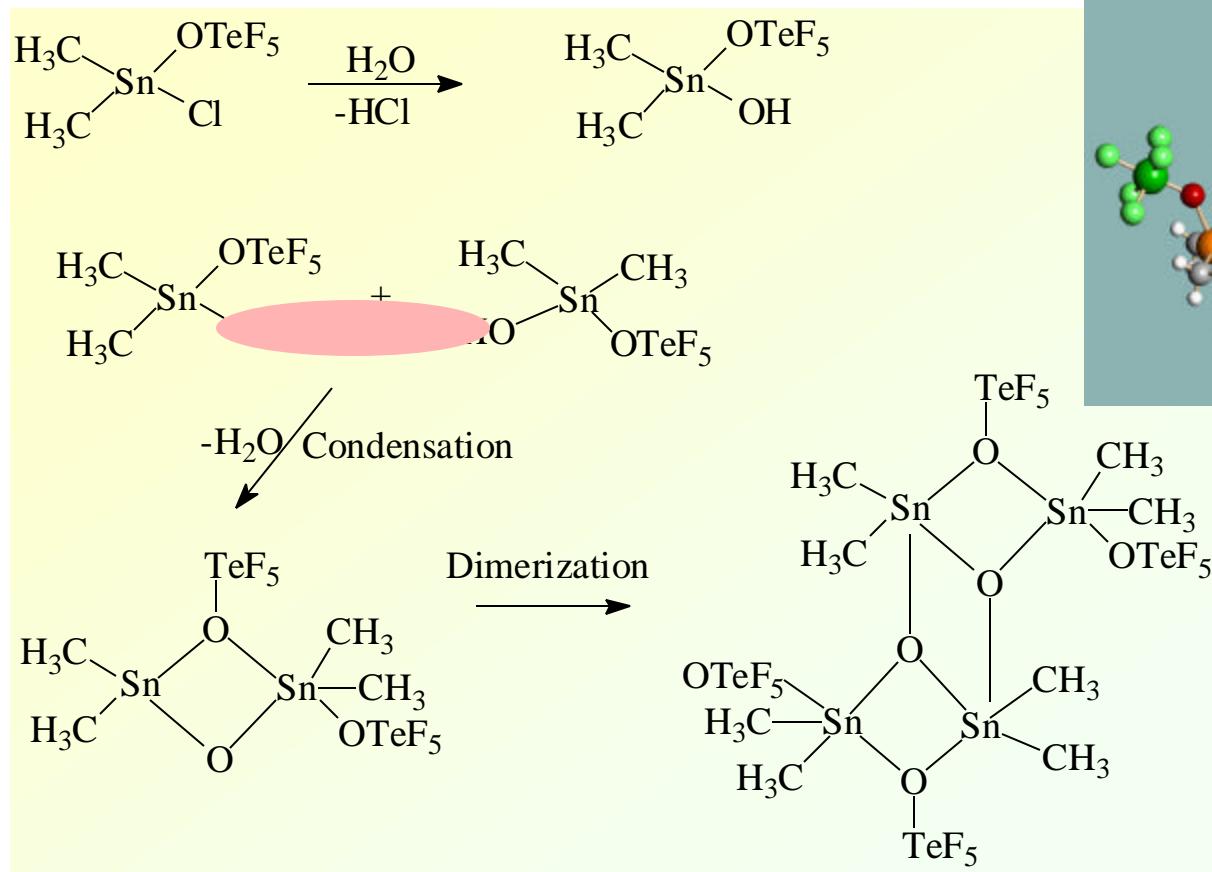
Sn-Cl contact found in the crystal lattice is 3.201(1) Å, which is much shorter than the sum of van der Waal radii of tin and chlorine. A longer Sn-Cl contact is also present at 3.904(2) Å.  
 $S(vdWSn + vdWCl) = 2.17 + 1.75 = 3.92 \text{ \AA}$



One Sn-F contact is also found in the crystal lattice 3.140(4) Å, which is much shorter than the sum of van der Waal radii of tin and fluorine.  
 $S(vdWSn + vdWF) = 2.17 + 1.47 = 3.64 \text{ \AA}$



# *Hydrolysis of the Sn-Cl bond in $(CH_3)_2Sn(Cl)OTeF_5$*



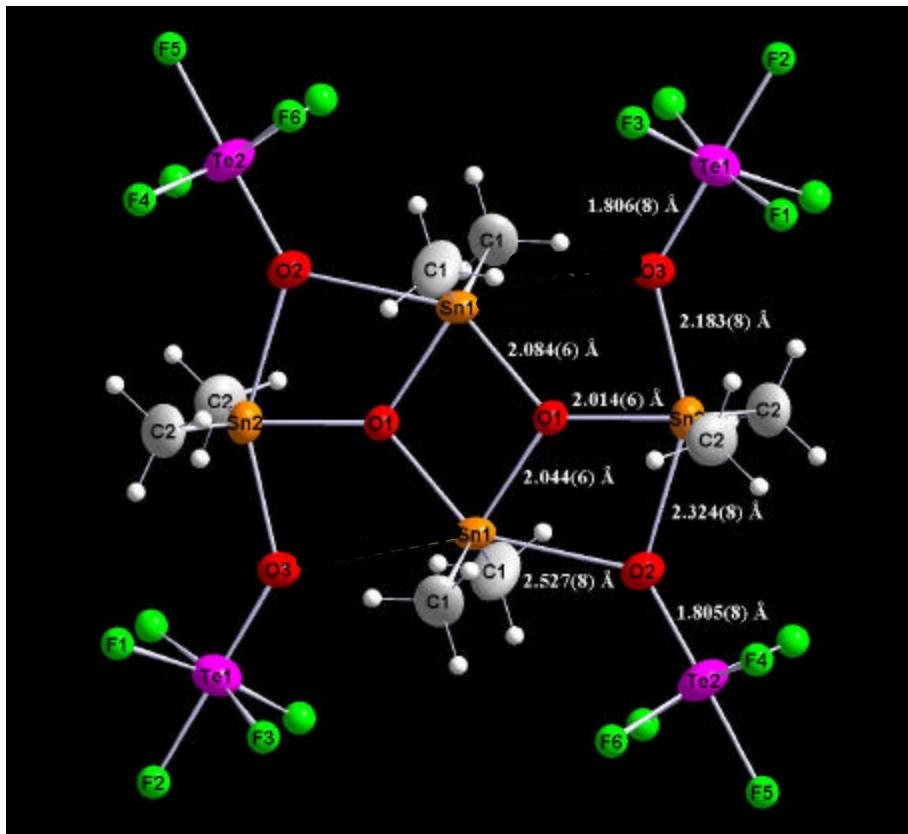
March 29, 2004

Award Symposium for Dr. Surya Prakash, 227<sup>th</sup> ACS National Meeting, Anaheim  
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# Structure of the dimethyloxotin(IV) teflate



Unit cell dimensions (Å)

Orthorhombic

Space Group: *Pnnm*

$a = 12.574(6)$ ,  $b = 12.667(6)$ ,

$c = 11.682(5)$

Volume (Å<sup>3</sup>) = 1860.6(1)

$Z = 2$

$T = 243\text{ K}$

$R1 = 0.0376$

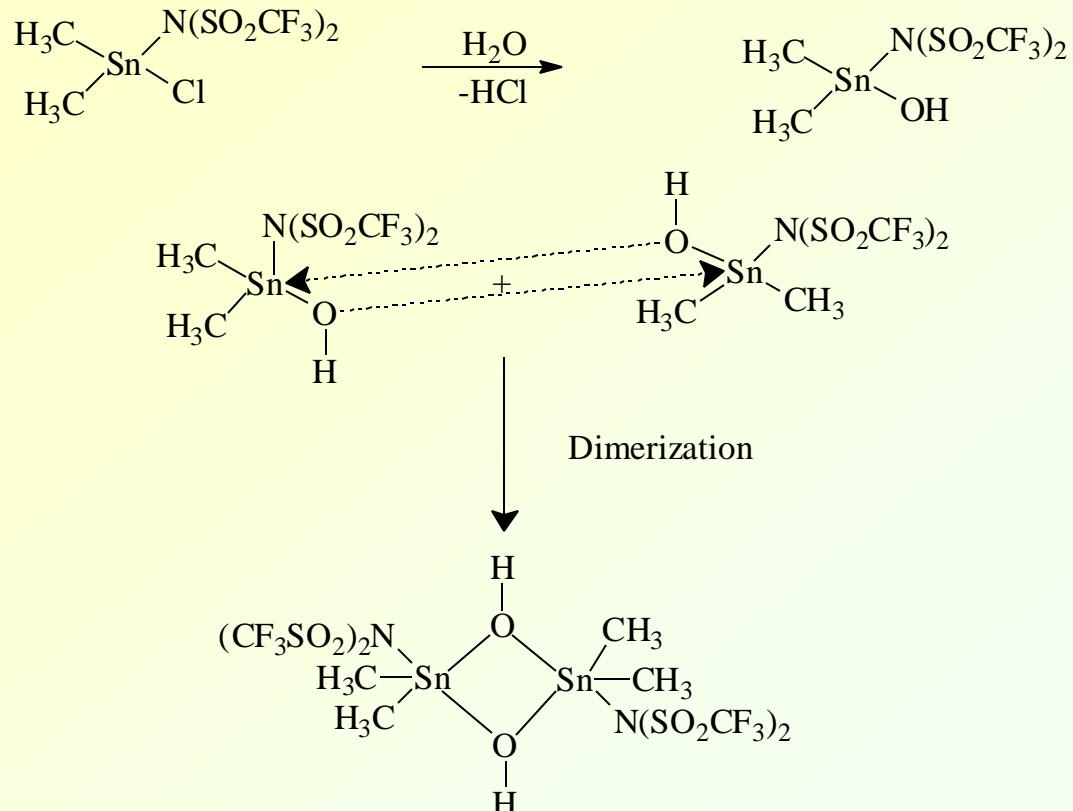
$wR2 = 0.1021$

$S = 1.04$

$$\begin{aligned} S_{(\text{vdWSn} + \text{vdWO})} &= 2.17 + 1.52 \\ &= 3.69\text{ Å} \end{aligned}$$

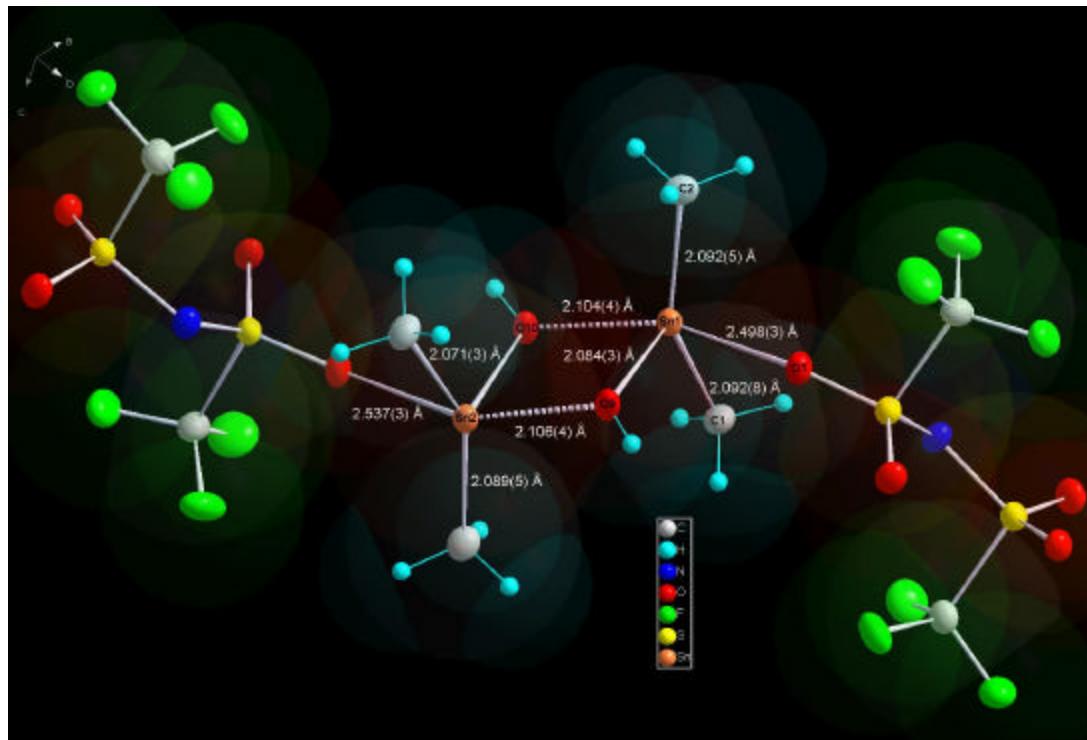


## Hydrolysis of the Sn-Cl bond in $(CH_3)_2Sn(Cl)N(SO_2CF_3)_2$





# Structure of $\text{Me}_2\text{Sn}(\text{OH})\text{N}(\text{SO}_2\text{CF}_3)_2$

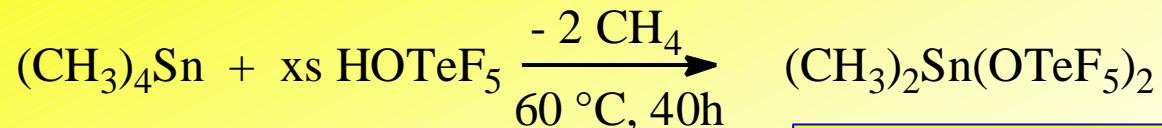




## Solvolytic synthesis of dimethyltin(IV) teflate

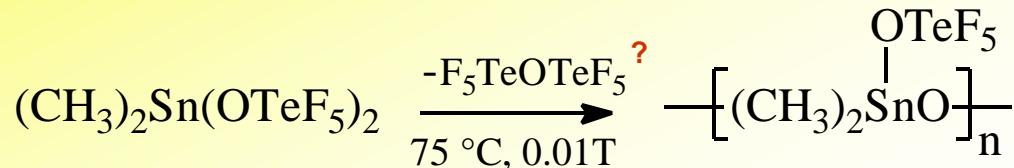


- ✓ Dimethyltin(IV) teflate is formed when tetramethyltin is reacted with excess teflic acid



MS shows  $[\text{M}-\text{CH}_3]^+$  peak

- ✓ Upon sublimation  $\sim 75^\circ\text{C}/0.01\text{T}$  a polymeric species is formed, probably due to the loss of  $\text{O}(\text{TeF}_5)_2$



$$n(\text{TeO}) = 877 \text{ cm}^{-1}; n(\text{SnO}) = 434 \text{ (IR) cm}^{-1}; n_{\text{as}}(\text{SnC}) = 591 \text{ cm}^{-1}, n_s(\text{SnC}) = 531 \text{ cm}^{-1}$$



# Structure of dimethyltinooxteflate



## Unit cell dimensions (Å)

Monoclinic  $P2_1/n$

*Rotational TWIN*

$a = 7.510(6)$ ,  $b = 15.729(12)$ ,

$c = 8.119(7)$

$B = 115.1(1)^\circ$

Volume (Å<sup>3</sup>) = 876.7(12)

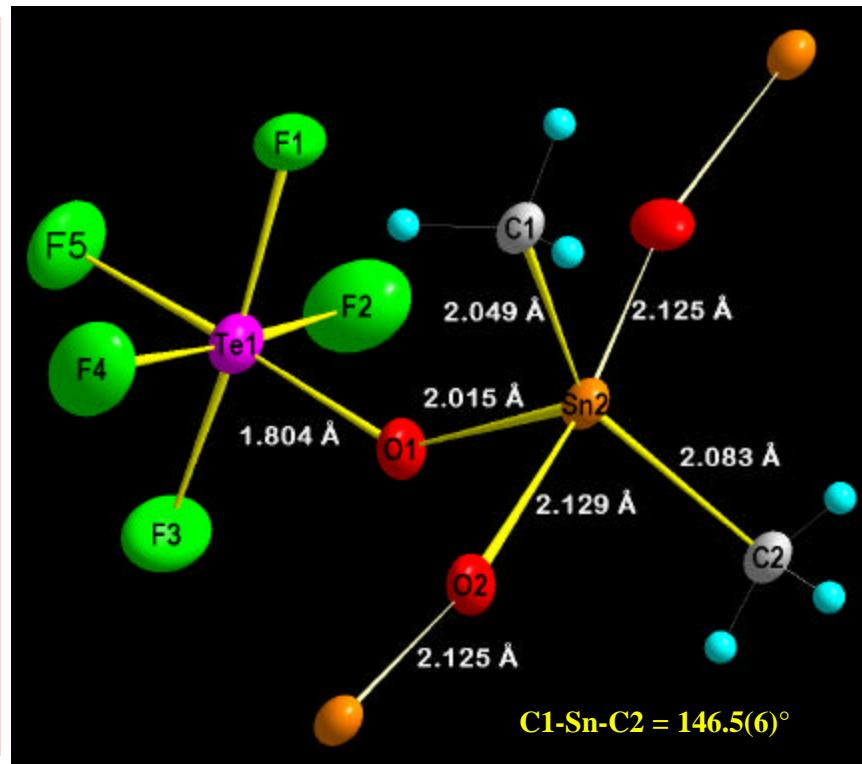
$Z = 4$

$T = 233(2) K$

$R1 = 0.1028$

$S = 1.84$

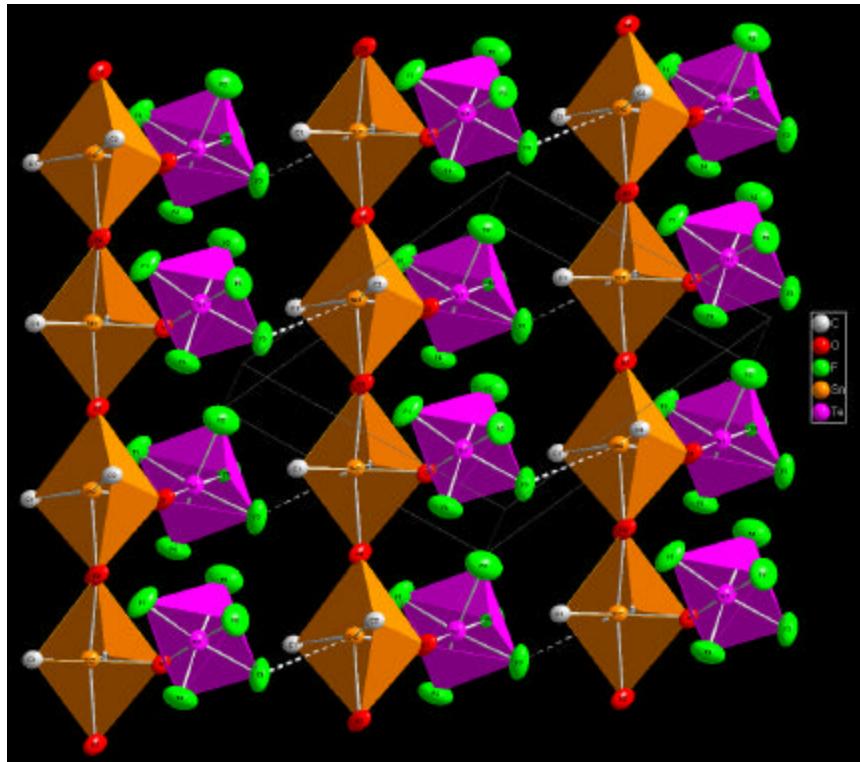
$\text{BASF} = 0.256$



$C1\text{-Sn}\text{-O}1 = 110.2(5)^\circ$ ;  $C2\text{-Sn}\text{-O}1 = 103.3(6)^\circ$ ,  
 $\langle \text{equi. X-Sn-X (av)} \rangle = 120^\circ$ ;  $O2\text{-Sn}\text{-O}2^* = 169.9(5)^\circ$



## Crystal packing showing tin and tellurium polyhedra



$$\begin{aligned} S_{(\text{vdWSn} + \text{vdWF})} &= 2.17 + 1.47 \\ &= 3.64 \text{ \AA} \end{aligned}$$

Sn-F distance in the crystal packing  
= 3.107(16) Å

The structure shows polymeric Sn-O chains bridged by a fluorine atom of the OTeF<sub>5</sub> group.

$$\angle \text{Sn-O}_2\text{-Sn}^* = 167.2^\circ$$

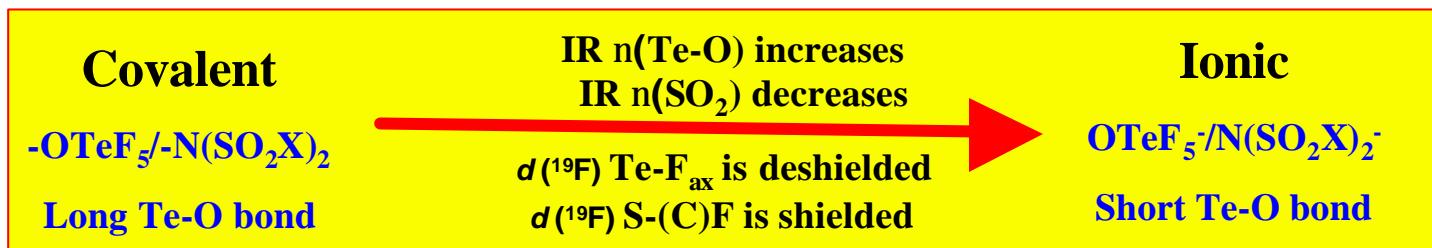
$$(\text{Sn}^* = \frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z)$$



## Conclusions



- Trimethyltin(IV) teflates/F-imides are highly electrophilic in nature and form 1:1 or 1:2 complexes with donor solvents
- $^{119}\text{Sn}$  NMR chemical shifts can reflect the “electrophilic strength” and relative anion basicity for a  $\text{Me}_3\text{Sn}$  (IV) compound.
- During the solvolysis of trimethyltinchloride in  $\text{HOTeF}_5$ , there is a preferential cleavage of the Sn-C bond versus Sn-Cl bond
- Chlorodimethyltin(IV) teflate hydrolyzes to form a Sn-O ladder compound and sublimation of dimethyltin(II) bis(teflate) results in the formation of an oxo-bridged species.





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## Bond distances and angles

### $\text{Me}_2\text{SnClOTeF}_5$



• Sn(1)-C(2)	2.104(4)	C(2)-Sn(1)-C(1)	117.8(2)
• Sn(1)-C(1)	2.115(4)	C(2)-Sn(1)-C(3)	120.1(2)
• Sn(1)-C(3)	2.120(4)	C(1)-Sn(1)-C(3)	122.1(2)
• Sn(1)-O(1)	2.306(3)	C(2)-Sn(1)-O(1)	89.83(15)
• Sn(1)-O(2)	2.335(3)	C(1)-Sn(1)-O(1)	92.3(2)
• S(1)-O(3)	1.427(2)	C(3)-Sn(1)-O(1)	87.19(13)
• S(1)-O(4)	1.428(3)	C(2)-Sn(1)-O(2)	91.04(15)
• S(1)-N(1)	1.573(3)	C(1)-Sn(1)-O(2)	90.8(2)
• S(1)-C(4)	1.825(5)	C(3)-Sn(1)-O(2)	88.95(13)
• S(2)-O(6)	1.421(3)	O(1)-Sn(1)-O(2)	175.94(11)
• S(2)-O(5)	1.433(3)	O(3)-S(1)-O(4)	118.5(2)
• S(2)-N(1)	1.589(3)	O(3)-S(1)-N(1)	107.6(2)
• S(2)-C(5)	1.844(4)	O(4)-S(1)-N(1)	116.1(2)
		O(3)-S(1)-C(4)	104.0(2)
		O(4)-S(1)-C(4)	105.4(2)
		O(6)-S(2)-O(5)	118.2(2)
		O(6)-S(2)-N(1)	109.0(2)
		O(5)-S(2)-N(1)	115.3(2)
		O(6)-S(2)-C(5)	104.7(2)
		O(5)-S(2)-C(5)	105.0(2)
		S(1)-N(1)-S(2)	125.3(2)